



# A Bright

*Livermore researchers perfect  
an electron microscope to study  
fast-evolving material processes  
and chemical reactions.*





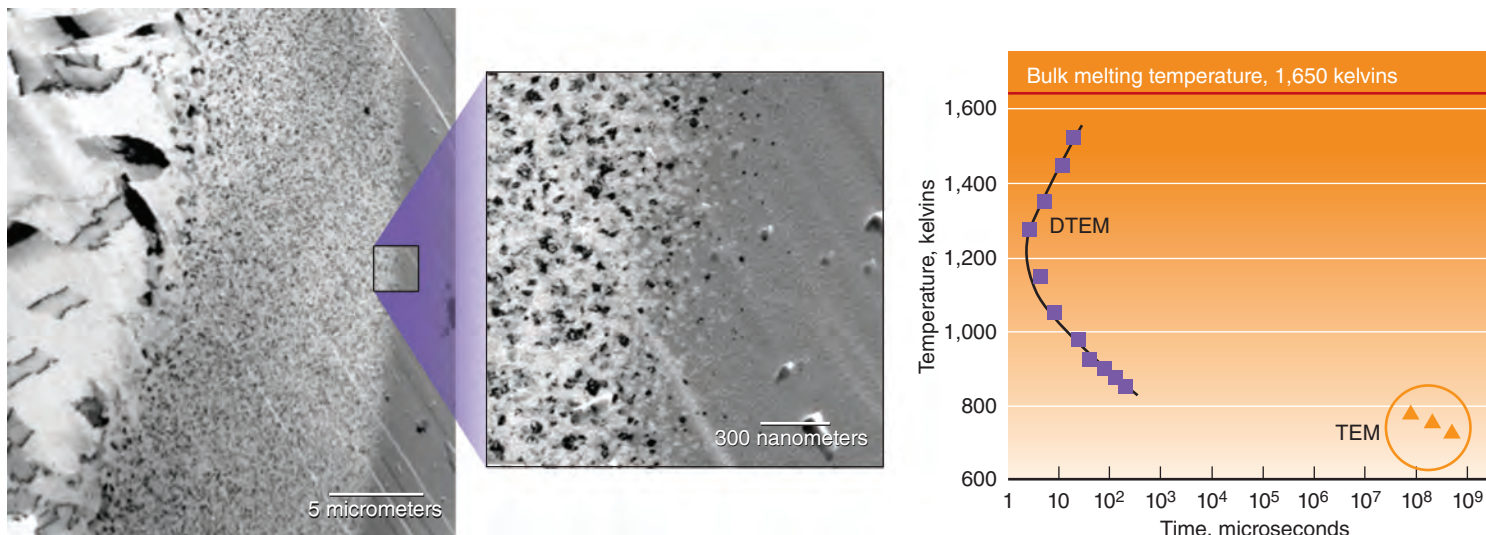
# Idea for Microscopy

**S**MALL objects tend to evolve over short timescales. In chemistry, biology, and materials science, a sequence of changes no more than a nanometer ( $10^{-9}$  meters) in size can pass by in a microsecond ( $10^{-6}$  seconds), leaving behind little evidence. Reconstructing these processes and determining how and why they took place can be as difficult as the task faced by crime-scene investigators piecing together evidence with no eyewitnesses to interview. Many techniques can record the static, before and after states of materials, but they lack the spatial and temporal resolution to capture the nearly instantaneous changes occurring in between.

Two complementary techniques emerging in the past decade provide precise, high-resolution images of many classes of fast-moving processes. One technique, the ultrafast electron microscope developed by Ahmed Zewail and colleagues at the California Institute of Technology, captures highly repeatable and reversible material processes, such as electronic phase transitions, by accumulating images during millions or billions of experimental iterations. The other approach is the dynamic transmission electron microscope (DTEM) designed by a team of Lawrence Livermore researchers. DTEM acquires sufficient information in a single experiment to generate a

Livermore researchers (above, from left) Bryan Reed, Melissa Santala, William DeHope, Thomas LaGrange, and Joseph McKeown operate the dynamic transmission electron microscope (DTEM), which captures magnified, short-exposure images of fast-evolving material behavior at the nanometer scale. Not pictured are Geoffrey Campbell, Glenn Huete, and Richard Shuttlesworth. The rendering on the opposite page shows a cutaway view of a DTEM optical column.





Micrographs (left and center) from an experiment exploring structural formation in metal alloys under extreme conditions show that rapid heating of a nickel–titanium film produces crystals in a range of sizes. DTEM enabled in situ observation of the material's structural evolution, revealing that a precarious balance between the crystal formation and crystal growth rates is responsible for this variety. DTEM data such as those in the graph (right) also help researchers examine how temperature influences the crystallization rate in regimes that cannot be measured with a standard transmission electron microscope (TEM).

high-resolution image of a micro- to nanosecond-long, nanoscale event. With DTEM, researchers can study irreversible events such as phase transformations, chemical reactions, and crystal growth.

DTEM builds on a staple research technique—the transmission electron microscope (TEM)—that for more than 50 years has provided information about material properties and structure down to the atomic level. TEM measurements are made at video frame rates (about 30 frames per second), which are thousands or even millions of times slower than the rate at which processes evolve in micro- or nanostructured materials. To capture dynamic behavior with a TEM, researchers must start and stop a process, which is not always feasible and rarely precise.

Livermore's work on DTEM was inspired by a presentation at the 2003 Conference on Frontiers of Electron Microscopy in Materials Science, in which a scientist from Oleg Bostanjoglo's laboratory at the Technical University of Berlin discussed preliminary work on a high-time-resolution TEM. After attending the talk and visiting the German laboratory, Livermore scientists Wayne

King and Geoffrey Campbell initiated an effort to develop a similar microscope. Bostanjoglo retired soon after, leaving Livermore as the sole research institution working on the concept.

With support from the Laboratory Directed Research and Development Program, Department of Energy Office of Science, and internal technology development funds, DTEM team members proved the technology's viability and significantly enhanced the original idea. The team also modernized the microscope platform and improved its spatial resolution from 200 nanometers to better than 10 nanometers. These modifications, spearheaded by Thomas LaGrange and Bryan Reed, ultimately earned the development team two R&D 100 awards (see *S&TR*, this issue, p. 2; November/December 2008, pp. 4–5), a Nano 50 Award, and a *Microscopy Today* Innovation Award.

### Enhancements with Laser Precision

A TEM operates on the same principles as a light microscope but substitutes electrons for light to achieve much higher resolution. Electrons emitted by a source

at the top of the microscope are focused by magnetic lenses into a narrow beam and directed through a thin specimen. Depending on the specimen's material properties—its density and crystalline structure, for example—some of the electrons are scattered and used to form an image or diffraction pattern. Subsequent lenses in the TEM column magnify this image or pattern onto a fluorescent screen. The resulting light and dark regions provide information about the materials examined—their crystalline grain structure, dislocations, or even single atomic rows and columns. A camera at the bottom of the microscope then records the data.

Conventional TEMs produce a steady stream of electrons that pass through the optical column one at a time. DTEM releases electrons in a single burst, with up to 1 billion electrons filling the column. Electron microscopes typically generate electrons through thermionic emission—in much the same way an incandescent bulb uses heat to produce light—or through field emission, which combines a metallic conductor and an electrostatic field. The electron source for DTEM is a metal cathode driven by an

ultraviolet laser. A pulse of light emitted by the laser enters the optical column and is reflected by a mirror onto the cathode. The cathode releases a burst of electrons that are accelerated toward the sample. The duration of the laser pulse determines the “exposure time” for recording the image or diffraction pattern. DTEM’s cathode has a large surface area for increased current generation. A flat tantalum disk mounted to a tungsten filament allows it to also operate in thermionic mode.

The electron pulse is propelled through a system of condenser lenses that precisely focus and point the beam. Conventional TEMs achieve the desired beam parameters using small apertures with lenses to discard all but a fraction of the current. The Livermore team redesigned the lens system to increase the number of electrons generated and boost spatial resolution. They added condenser lenses and an extra focusing (crossover) region and reduced the number of apertures—a design that maximizes electron throughput while focusing the beam down to a small spot on the sample. As a result, DTEM produces a brighter, higher current beam than a conventional TEM, with little sacrifice in beam coherence (which affects image contrast and diffraction-pattern sharpness). In addition, researchers can adjust the lens’s focal length to control how much of the beam is used in an experiment.

DTEM has an unusually precise, adjustable, and powerful heating element—a pulsed laser—for initiating the dynamic process to be probed, yielding temperatures and heating rates far beyond those offered by a standard TEM. The specimen drive laser is synchronized with the cathode laser to control the time that elapses between heating and the electron pulse arriving at the sample. The programmable laser also allows researchers to specify the conditions for initiating a material process.

Instead of heating an entire sample at once, DTEM confines heating to an area less than 100 micrometers across,

enabling users to isolate both fast and slow reactions. For instance, at high temperatures, many metals undergo phase transformations within picoseconds ( $10^{-12}$  seconds) to microseconds, while oxidation occurs more slowly. The gradual, uniform heating available in a conventional TEM cannot separate the two processes. With DTEM’s specimen drive laser and nanosecond acquisition rates, researchers can quickly heat a sample, capture transformations before the sample has time to oxidize, and compare those results to the properties of an unheated sample.

To develop DTEM, the Livermore team modified an existing TEM platform. “One challenge was that these systems were not designed for modification,” says Reed. “We kept our changes as noninvasive as possible.” Space within the optical column was extremely limited, and existing systems were surrounded by magnetic, radiation, and vacuum shielding that could not easily be breached. Lasers and other new components also had to be engineered to work seamlessly with original equipment. Fortunately, the microscope manufacturer, JEOL, provided instrument drawings and measurements to help with the design efforts.

### DTEM in Action

DTEM supports an array of Livermore research programs and collaborations with universities and industrial partners to study fast material processes ranging from phase transformations to chemical reactions and nanostructure growth. Interest in the device continues to grow, especially in the areas of materials science and microscopy.

In one such effort, materials scientist Joseph McKeown and collaborators from the University of Tennessee at Knoxville and Oak Ridge National Laboratory are evaluating methods to control the size and spacing of metal and alloy nanoparticles for biomolecular and chemical sensors. This project uses DTEM’s sample drive laser to melt nickel samples into a liquid film just 5 to 10 nanometers thick. Intermolecular

forces and surface tensions break up, or dewet, the ultrathin film, causing it to ball up before recrystallization. DTEM imaging and diffraction capabilities have helped the researchers understand the mechanisms that control dewetting and how this process affects particle size and spacing in the recrystallized material.

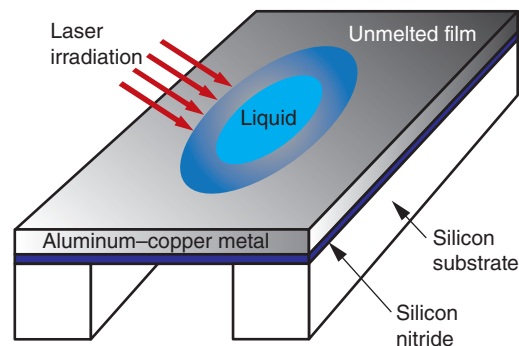
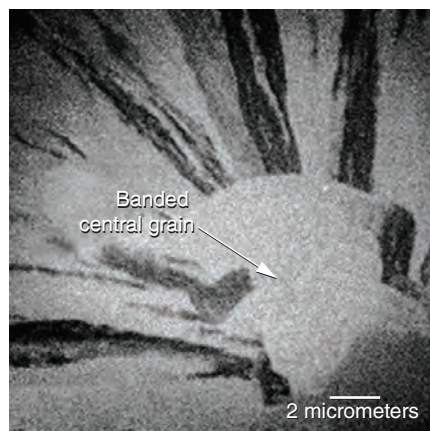
LaGrange and McKeown have also been working with colleagues at the University of Pittsburgh to understand rapid solidification in nanostructured metals, which is important in certain additive manufacturing processes. For this project, they are examining aluminum–copper, a classic alloy for solidification research, using an experimental configuration that allows them to measure previously inaccessible nanoscale dynamics under melt conditions. DTEM’s laser energy produces a melt pool bounded by cooler solid walls of unmelted film. The liquid alloy resolidifies in tens of microseconds, producing distinct zones with unique microstructural features. As solidification progresses, the solid–liquid interface accelerates until an oscillatory instability develops. DTEM images show that this instability changes solid-material growth patterns, yielding large grains with a banded structure.

Using those results, the team plotted how quickly the reaction front is moving and tied its acceleration to temperatures, structures, and instabilities observed in the material. “What we found agrees very well with previous results involving aluminum–copper alloys,” says McKeown. “Our results indicate that the DTEM technique is viable. Now, we can turn away from model systems and focus on those we know less about, with confidence that DTEM produces reliable results.”

### Nanoscale Movie Magic

LaGrange and McKeown performed their experiments in DTEM’s single-shot mode, which captures one instance of a process. Single-shot experiments are repeated on fresh specimens as often as

DTEM researchers studied the structural evolution of aluminum–copper thin films solidified at greater than 1 meter per second—a rate far too fast for other imaging techniques to capture at high resolution. At such speeds, instabilities can develop at the solid–liquid interface, leading to unique microstructural features such as the banded region in the micrograph at left, which appeared about 25 microseconds after heating.



required, each with a different time delay, and the collection of images are combined into an averaged view of the process over time. An averaged view is sufficient for studying reactions that are nearly identical every time. To scrutinize more complex or variable behavior, such as a branching growth front or phase transformation initiated from many sites, researchers need a system that can capture multiframe movies rather than single snapshots. A major enhancement to DTEM, completed in 2012, provides that capability.

Movie-mode DTEM (MM-DTEM) can record nine complete images or diffraction patterns in 2 microseconds, with variable delay between the frames, enabling the in-depth study of an individual, irreversible process. Even for highly repeatable reactions, movie mode can help researchers determine the full event sequence and the rate at which changes occur.

In movie mode, after a laser pulse initiates the material process, a series of laser pulses hits the cathode and generates an electron pulse train. The train passes through the sample, and a deflector, synchronized with the laser system, diverts each pulse onto a different region of a camera that is sensitive enough to image individual electrons. The camera stores the data in on-chip buffers that are read out after the experiment and segmented into

frames. To make movie mode possible, the researchers upgraded the laser hardware and software and added the deflector to direct images onto the camera.

DTEM's electron-generating laser, the star of movie mode, was designed to be more programmable, flexible, and durable. LaGrange initially contacted several laser manufacturers but could not find one to build the laser system as envisioned. Undaunted, DTEM team members built it themselves, using a combination of custom and commercial components and advanced techniques borrowed from the National Ignition Facility's injection laser system. Livermore engineer Andy Bayramian, DTEM team member Glenn Huete, and researchers at the aerospace company Northrop Grumman provided expertise for achieving the smooth beam profile required to generate a desirable electron pulse.

With the upgrades, the laser pulses that create the electron pulses can last from 10 nanoseconds to 1 microsecond, and frame spacing can range from 50 nanoseconds to 150 microseconds. The component that enables researchers to define an experiment's timescale and tailor the laser parameters accordingly is the arbitrary waveform generator (AWG), a cost-effective adaptation of a Livermore-developed fiber laser technology. AWG's optical modulator controls the laser pulse

spacing, shape, and other details, enabling unprecedented temporal ranges.

AWG's benefits do not end there. With so many electrons packed into DTEM's relatively tight pulses, electrons in the microscope column frequently collide with and repel one another, potentially degrading image resolution. For example, information encoded in the trajectories of individual electrons as they pass through a specimen can be lost when those electrons later bounce off one another. The affected electrons reform their pattern in a different way on the imaging screen, causing stochastic blurring of the resulting image—a difficult problem to mitigate.

Electron–electron interactions can also disperse the electron pulse. The electron optics in DTEM partially compensate for this type of blurring. In addition, AWG can temporally shape the pulse to minimize these effects in the electron gun and increase brightness.

Electron repulsion effects essentially set the lower limit for the spatial resolution of DTEM as currently designed. Fortunately, not all experiments require nanosecond time resolution. AWG offers the ability to trade off spatial resolution and exposure time. Experiments designed to study somewhat slower processes, such as certain catalytic reactions and crystallization, can use longer pulses and thus exposure



times. Because long pulses experience fewer electron interactions than short ones, they can generate more electrons to boost the signal and spatial resolution. Even the longest pulses produced by DTEM are four orders of magnitude better in temporal resolution than the pulses from a conventional TEM.

Another movie-mode advance is an accurately timed, high-speed electrostatic deflector array in which four high-voltage switches connected to customized deflectors are inserted into the projector lens below the sample. The switches deflect each image to a different part of the camera, thereby overcoming the camera's multisecond refresh rate. The current design creates nine frames with 512- by 512-pixel resolution, but other arrangements are possible.

A programmable electronic timing and control system orchestrates MM-DTEM

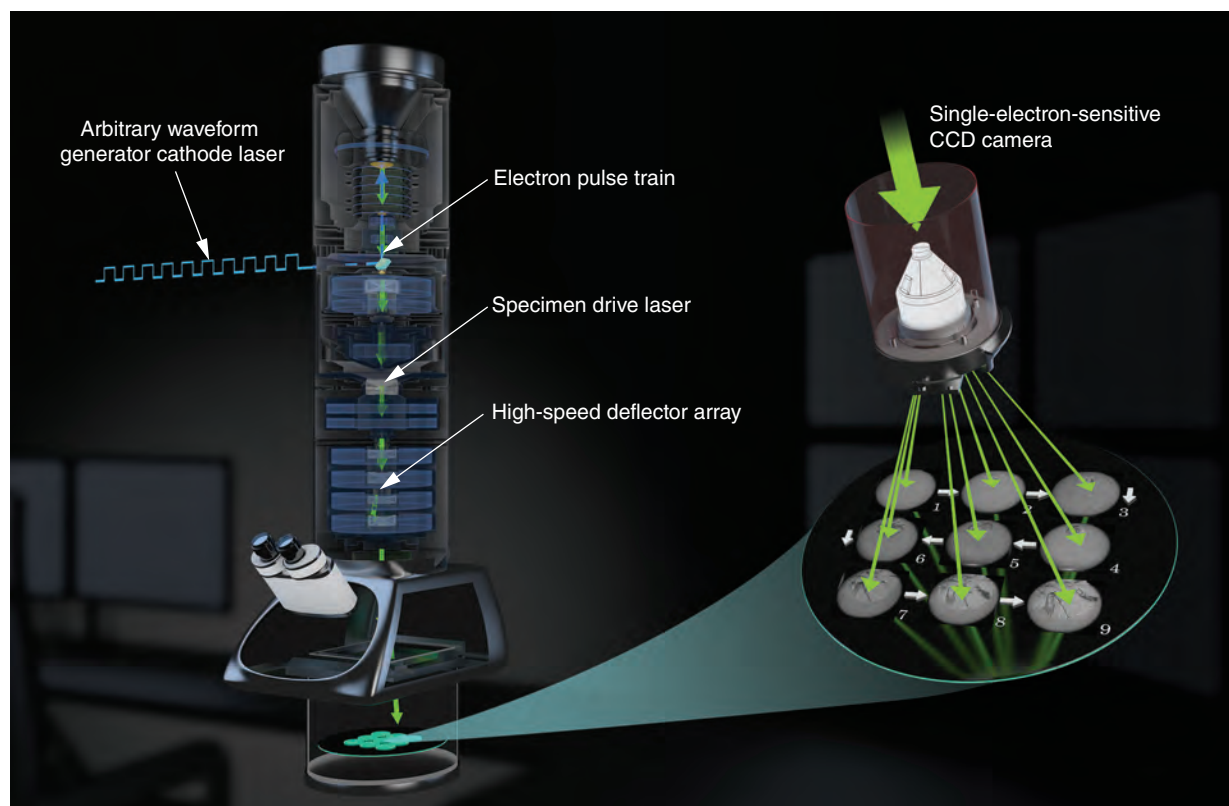
operations. Livermore-developed software integrated into a digital timing system allows users to define the pulse requirements, such as the start and end times for each exposure, and to control AWG, the specimen drive laser, deflector, diagnostic and alignment components, and camera. The system synchronizes component operations to within 1 nanosecond.

### Crystallizing Material Behavior

With MM-DTEM, researchers can watch the formation, movement, growth, and interaction of individual crystal grains, defects, phase fronts, and chemical reactions. They can also gather more data in fewer experiments, which is especially helpful when specimens are difficult to obtain or time consuming to prepare. Reed adds, "In materials science, reactions often happen quickly and then slow down.

With movie mode, we can tailor the image spacing and exposure time to focus on the important events. We can also get a high-resolution image of the 'before' state—what the sample is like immediately before the laser drive hits it."

One series of MM-DTEM experiments captured fast-moving chemical reactions in reactive multilayer foils (RMLFs), commercial products used for applications that require rapid, local deposition of heat, such as joining microelectronic components. RMLFs are made by alternating nanoscale layers of metals that, with a jolt of laser energy, will react to form an intermetallic compound. The layers undergo a series of material changes—mixing, melting, and resolidifying—all in less than a microsecond. Optimizing an RMLF for a particular application requires a thorough understanding of the timing and sequence



The current DTEM design includes two pulsed lasers, a sophisticated timing and control system, a high-speed pulse deflector, and a high-resolution, charge-coupled-device (CCD) camera on the optical column of a standard TEM. With these modifications, DTEM can record high-time-resolution, nanometer-scale images in both single-shot and movie mode.

of material changes and other parameters that researchers had been unable to measure. “If we’re using the foil to join two materials, we need to know how much energy is released and what the heat loss mechanisms are,” says LaGrange.

Campbell and LaGrange worked with colleagues from Johns Hopkins University and Sandia National Laboratories on a diffraction and imaging project that used MM-DTEM to study mobile, high-temperature reaction zones in nickel–aluminum and titanium–boron RMLFs. In the nickel–aluminum experiments, movie mode revealed a brief and unexpected liquid phase, the surprisingly fast formation of large crystalline grains, and a short phase separation during cooling. The transient liquid phase left no trace once it disappeared, but knowing of its existence allowed the researchers to correctly interpret solidification rate information.

The titanium–boron investigations revealed a sharp, smooth reaction front moving at a constant speed—essential details for assessing foil reliability. Large single-crystal grains of the intermetallic material appeared almost immediately after the front arrived and then evolved only minimally, despite the extremely high local temperature.

Before the MM-DTEM measurements, computational models used for RMLF design were relatively ineffective at predicting foil behavior. The Livermore collaboration showed that these material changes play a significant role in moving heat, mixing material, and relaxing the structure, all important parameters for predictive modeling. MM-DTEM also improved the accuracy of reaction speed measurements from 20 percent to within 1 percent. Researchers discovered that the reaction front for a nickel–aluminum

RMLF, for instance, moves at the astonishing rate of 13 meters per second.

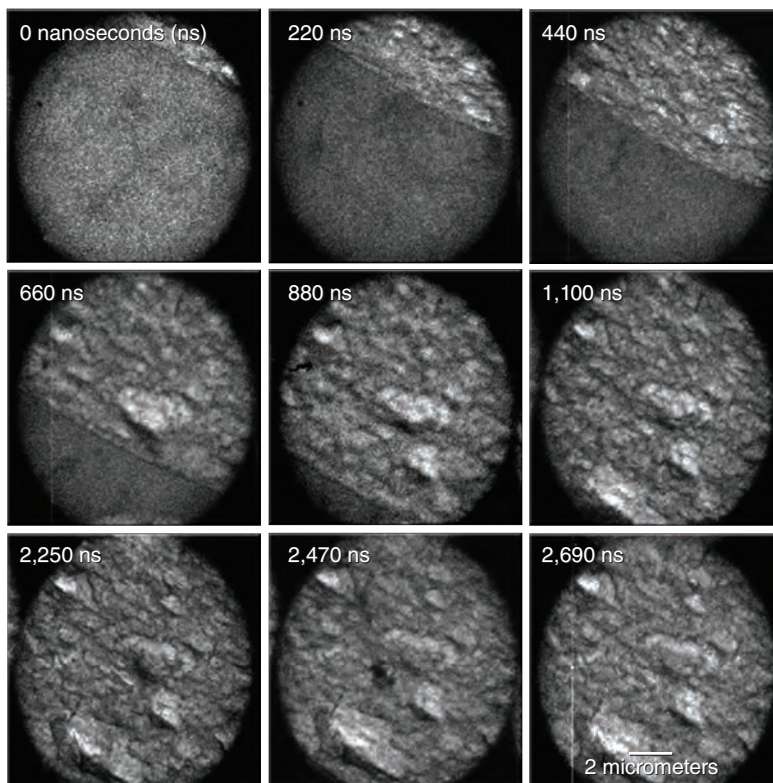
One project that showcases movie-mode benefits involves phase-change materials (PCMs), which provide memory for digital storage applications and thus have strict performance requirements. During write and erase processes, PCMs must switch between amorphous and crystalline phases within nanoseconds, processes controlled through rapid changes in temperature. However, the materials must remain stable for years at a time to preserve stored information. Scientists want to better understand how different PCM alloys crystallize and confirm that existing models accurately predict material behavior over large ranges of time and temperature.

Laser-induced crystallization of amorphous PCMs occurs on nanosecond and nanometer scales and thus is difficult to measure. Crystallization experiments have been performed at lower temperatures, where crystallization proceeds more slowly and microstructural and temperature changes are more easily monitored. Unfortunately, crystal formation and growth rates are temperature dependent, so extrapolating material behavior from the limited data at low temperatures can be tricky.

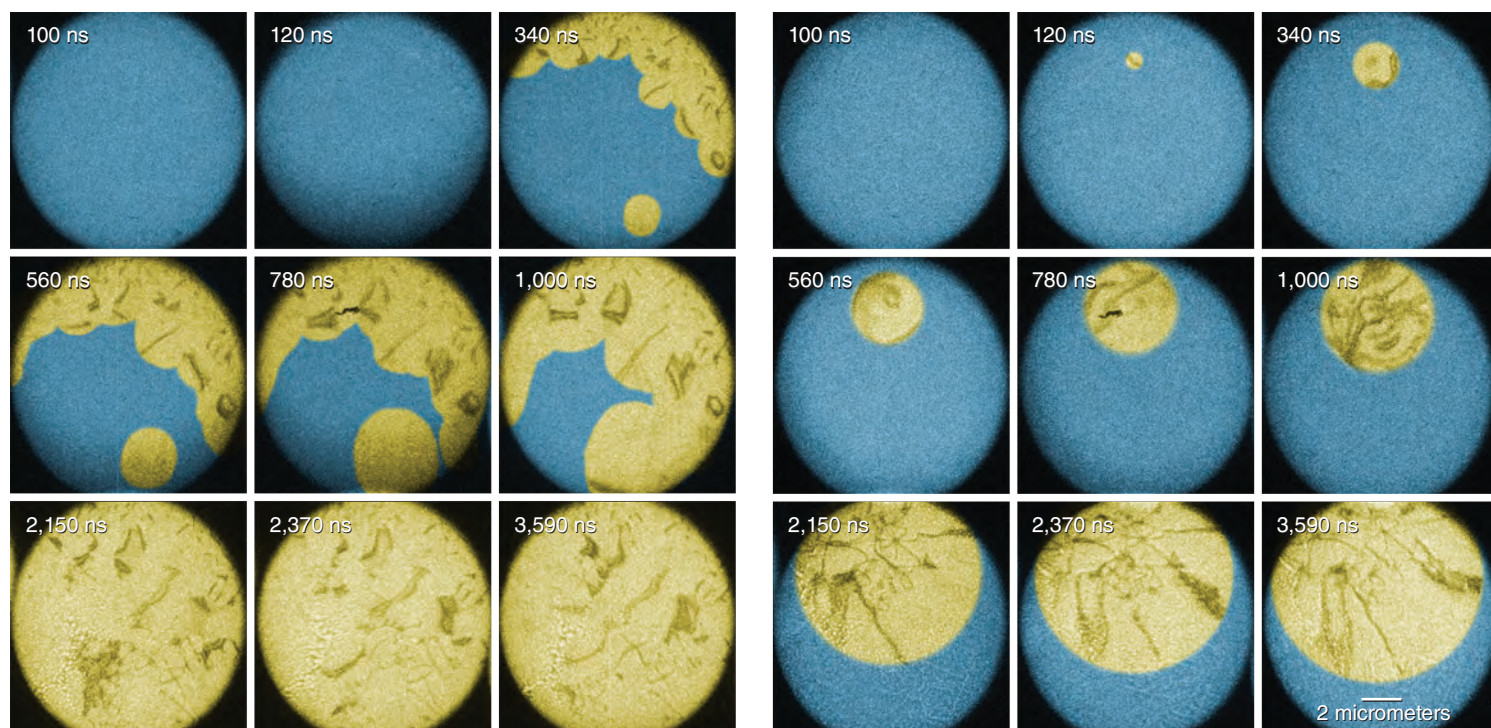
Once again, DTEM resolves these problems. Laboratory scientist Melissa Santala and her Livermore colleagues worked with researchers at IBM using DTEM in both single-shot and movie mode to study the nucleation and growth of single crystal grains of a germanium–tellurium alloy during rapid laser crystallization.

Crystal formation and growth do not proceed identically from experiment to experiment. Crystals form in different locations each time and develop differently. With movie mode, the research team tracked the growth of single germanium–tellurium grains and accurately measured how fast a grain grew at each point.

Nine DTEM movie frames record behavior occurring in a titanium–boron reactive multilayer film. A thin, dark line at the reaction front indicates the likely presence of a liquid phase. The line thickness and the reaction front velocity allow for precise measurement of the liquid’s short lifetime.







False-color DTEM movie frames from two experiments illustrate rapid crystallization (yellow regions) of amorphous germanium–tellurium (blue).

The experiments yielded sufficient information for determining crystal formation and growth rates, which affect how quickly a bit can be switched. In some instances, as a crystal grew, material ahead of the growth front started to melt because the crystallization process released energy and further heated the alloy. Using experimental data and computer modeling, the researchers also determined the approximate temperature at which crystallization occurred. Precisely connecting temperature with material behavior is crucial for understanding a material's crystallization properties and for optimizing computer storage devices.

### From One to Many

Within a few years, DTEM has demonstrated its efficacy at exploring irreversible nanoscale material processes

and providing insights into controlling these processes and material properties. The range of potential applications is just starting to emerge as the technology becomes more widely adapted. For instance, DTEM is a promising tool for biological research. Standard TEMs image biological samples in a fixed or frozen state, and although a light microscope can view life processes, it has only one-tenth of DTEM's spatial resolution. DTEM should be able to capture high-resolution images of biological events in liquid water such as protein binding and host–pathogen interactions. The Livermore device can also explore material behavior in atmospheric environments, as opposed to under vacuum.

The Laboratory has partnered with Integrated Dynamic Electron Solutions (IDES) to make DTEM technology broadly available to the scientific community. The product received a

Federal Laboratory Consortium Award for outstanding commercialization success in 2012. Laboratories in Europe, Canada, and Japan are investing in DTEM instruments and working with Livermore experts to implement the IDES hardware in their facilities. Says Campbell, “We want to see this technology spread and flourish.”

—Rose Hansen

**Key Words:** arbitrary waveform generator (AWG), crystallization, dynamic transmission electron microscope (DTEM), electron pulse train, electrostatic deflector, material science, movie-mode DTEM (MM-DTEM), phase-change material (PCM), reactive multilayer foil (RMLF), stochastic blur, transmission electron microscope (TEM), ultraviolet laser.

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